

Paper No. 27

FACILITY FC

(PAGES)
TMX-66942
(NASA CR OR TMX OR AD NUMBER)

(CODE)
18
(CATEGORY)

THE PHOTO-RESPONSE AT AN ALKALINE PAINT INTERFACE
WITH ALUMINUM

Walter A. Wappaus¹

REFERENCE: Wappaus, Walter A., "The Photo-Response at an Alkaline Paint Interface with Aluminum," ASTM/IES/AIAA Space Simulation Conference, 14-16 September 1970.

ABSTRACT: When a spacecraft coating comprised of aluminum oxide and potassium silicate is applied to an aluminum alloy (6061) substrate and subsequently partially coated with evaporated gold electrodes, a measurable potential is developed between the substrate and the gold electrodes. This effect is observed when the coating is in darkness and in vacuum. A dark current is also observed. Prior to observation, the specimen is heated in vacuum to 150°C for 24 hours.

When the coating is irradiated in situ with UV shorter in wavelength than 3600 Angstroms, the current and voltage is found to increase. Upon exposure to prolonged irradiation this current level decays exponentially with time. The voltage similarly decays with time in an exponential manner indicating that photo-degradation of the electronic transport properties is occurring.

The transport mechanism proposed to account for this behavior is a migration of protons toward the aluminum substrate and negative hydroxyl ions toward the gold electrodes resulting in the electrolysis of water in the coating. In the presence of UV this process is accelerated resulting in an increased current flow of three orders of magnitude. Since the current flow during UV radiation decays exponentially, this suggests a diffusion limited process.

KEY WORDS: alkaline paint, conduction of paints during ultraviolet exposure, electrode potential of paints, photo degradation, thermal control coatings, ultraviolet degradation

¹Goddard Space Flight Center, Greenbelt, Maryland 20771

INTRODUCTION

The stability of spacecraft coatings has been the object of much investigation. For successful satellite application a coating must exhibit stable properties for long periods of time when subjected to a space environment. One parameter, important to thermal control of a satellite is the absorptivity, or α , of the spacecraft coating. α is an optical property and usually changes when the coating is subjected to a space radiation environment. The object in coating formulation is to prepare a compound such that its time rate of change of α is very small when subjected to space radiation. The coating studied in this investigation, a mixture of aluminum oxide and potassium silicate, is stable with respect to α in a proton and electron radiation environment. However, it is unstable when subjected to ultraviolet irradiation. An attempt is made here to study the conduction characteristics of this coating by monitoring some electrical parameters of this coating while being subjected to ultraviolet radiation. This paper discusses an in-situ method for recording the behavior of a voltage across and a current through the thickness of a spacecraft coating applied to an aluminum alloy (6061) substrate. This coating when sprayed on an aluminum alloy substrate is representative of a typical spacecraft skin whose surface is painted for thermal control purposes.

In this paper conduction schemes are suggested and a model for ultraviolet degradation is proposed. As far as is known this particular approach in studying the in-situ degradation of spacecraft coatings has not been previously employed.

EXPERIMENTAL PROCEDURE

The coating which is discussed here is formulated from 1.0 micron alpha phase aluminum oxide² and potassium silicate³ mixed in a four to one solid ratio; that is,

$$\frac{\text{Weight Al}_2\text{O}_3}{\text{Weight K}_2\text{O} + \text{Weight SiO}_2} = 4$$

The mole ratio of SiO₂ to K₂O is 3.3; i.e.,

$$\left(\frac{\text{SiO}_2}{\text{K}_2\text{O}} \right)_{\text{mole}} = 3.3$$

²Manufactured by the Linde Division, Union Carbide Corp.

³Sylvania Corporation's electronic grade PS-7.

The pH at this ratio is 12.8 using water as the solvent. The preparation is sprayed on an aluminum alloy disc to a layer thickness of about 0.1mm. When air dried this coating has good hiding properties as well as low absorptivity values.

A set of gold electrodes is evaporated on the surface of a coated disc. The electrode configuration is shown in Figure 1. The disc is then mounted in a specimen holder which is designed to position a heater in contact with the uncoated side of the specimen. The heater is electrically insulated from the aluminum disc. The specimen holder firmly positions electrodes contacting the evaporated gold on the coated surface. A small amount of silver paste serves to insure electrical continuity between these contacts. The holder is mounted in a vacuum chamber such that it is electrically insulated from the chamber. An ultraviolet transmitting quartz port is provided through which radiation from a 500 watt medium pressure mercury lamp⁴ is directed normally onto the coated surface.

The two independent gold surface electrodes are electrically joined and connections are led outside the vacuum chamber via an electrical feed through. Another lead is attached to the aluminum substrate disc of the coated specimen and led externally in a similar manner. These two leads permit electrical measurements to be made across the coating layer.

The vacuum is ion pumped and capable of reaching the 10^{-9} torr region when empty. A sorption pump is used for roughing. All metal components are stainless steel. A light proof enclosure fitted with a shutter is placed over the quartz port and optically aligned with the ultraviolet beam. The specimen is in total darkness when not being irradiated with ultraviolet light. The pumping system and the light source are shown in Figure 2.

The radiation tests are designed to show the change of electrical parameters of the coating specimen as a function of total irradiation exposure time. At the start of the experiment the chamber containing the specimen appropriately mounted in the holder is roughed out and subsequently pumped down to the 10^{-6} torr region. The specimen is then heated to 150°C for a 24 hour interval and then allowed to cool. The pressure usually lowers to 10^{-7} torr after this procedure. The mercury ultraviolet source is positioned so that the specimen receives a one sun irradiance. The shutter is opened for a given time interval. The current and voltage are measured prior to and at the very beginning of the radiation time interval. Both light and dark current and voltage measurements are recorded with an electrometer.⁵

⁴Hanovia model 6730A10

⁵Keithley Instruments, Inc., Model 610B

At the conclusion of the irradiation time interval the shutter is then closed and a period of time is allowed to elapse before the next radiation interval in order to allow the specimen to return to initial temperature conditions. This cooling interval varies according to the length of time of radiation exposure, as the radiation interval is increased the cooling interval is also increased.

RESULTS

It is observed that, with the coating in darkness, a current flows through the paint compound. The sense of this dark current in the external measuring circuit is from the aluminum substrate electrode to the evaporated gold electrode. The dark current, when measured just prior to each radiation interval, was in the 10^{-12} ampere region for the duration of the experiment. A dark voltage is also observed and is developed across the two different electrodes. The gold evaporated electrode is of positive polarity. The dark voltage when measured just prior to the start of the experiment was found to be 0.35 volts. This dark voltage decreased linearly with time to a final value of 0.15 volts at the conclusion of the testing.

The results of the photo-response are presented in graphic form in Figures 3 and 4. Figure 3 shows the relationship between the current flowing through the coating, while being irradiated with ultraviolet light, versus the total accumulated time of this radiation. The time as plotted is the cumulative sum of the radiation intervals. Similarly, Figure 4 shows the relationship between the voltage developed across the coating electrodes, while being irradiated with ultraviolet light, versus the total accumulated time of radiation.

When a blocking filter was put into the light path, filtering out radiation of wavelength less than 3600 \AA , no photo-response was detected. The original color of the coating was a chalk white, but at the conclusion of the irradiation the color had changed to a light brown. Upon re-exposure to light and a normal laboratory atmosphere for several months, the color of the coating did not bleach but remained brown.

DISCUSSION

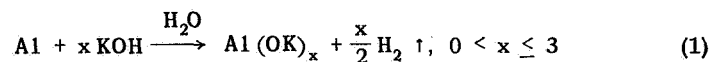
The coating material in contact with the aluminum substrate exhibits properties similar to a dry cell battery with a power output less than 10^{-12} watts. The voltage which is built up and maintained across the electrodes seems to occur spontaneously without the need for the application of an external voltage to initially polarize the system.

Contact potentials are certainly contributing to the voltage build up but their contributions are small compared to the total voltage in the dark condition.

The mechanism for current production in the coating is different during the dark and illuminated conditions. In order to discuss these conduction schemes it is necessary to describe the various anodic and cathodic reactions occurring under these different conditions. The following reactions are suggested to account for the conduction mechanism.

Dark Conduction

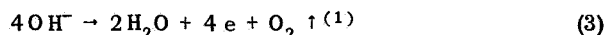
In considering a reaction at the cathode, one that is immediately suggested is,



due to the fact that the coating is strongly alkaline. Guided by (1), with the release of hydrogen at the cathode, the following competing cathodic reaction is also suggested,



The protons, which are furnished by dissociated H_2O , migrate toward the aluminum. At the gold anode the following reaction is suggested:



complementing (2). Here the hydroxyl ions migrate toward the gold electrodes releasing electrons for current flow in the external measuring circuit, accompanied by the release of oxygen as a gas. The hydroxyl ions are supplied by dissociated KOH or H_2O . In consideration of the K^+ ion and its migration to the cathode an equation similar to (2) may be written, resulting in a greater capacity for hydrogen formation. Reaction (1) is diminished as the water content of the coating is depleted. The conduction is ionic, resulting in the increased ionization of water at the cathode. The rate of these reactions determines

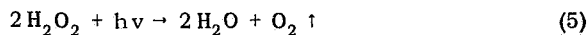
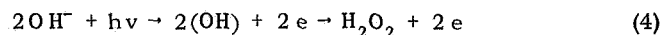
⁽¹⁾The numbers in parenthesis refer to the list of references appended to this paper.

how many electrons are furnished for current flow in the external measuring circuit but the mobility of the ions in the coating limits the conduction process.

Light Conduction

The above processes in the coating occur also during the illuminated condition but these are dominated by an additional reaction which supplies a much greater source of current.

Since the photoresponse was detected at wavelengths less than 3600 Å an energy threshold greater than 3.4ev is required for photo-conduction. A suggested reaction for this photo-conduction at the anodic surface is



Here additional electrons are provided for external conduction and additional gas is evolved. The cathodic reaction is the same as in (1) and (2).

A contributing mechanism suggested for increased conduction in this condition is that the OH forms an amorphous-like valence band permitting hole conduction.⁽²⁾

It is further suggested that reactions may still occur to provide conduction even if all the water is depleted by electrolysis. The following reactions are speculated:



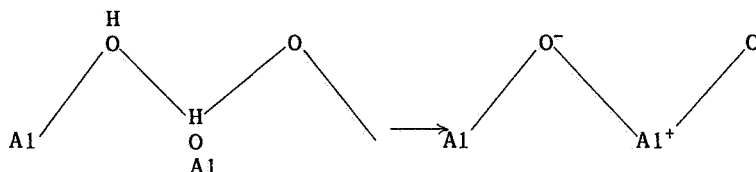
During the photo-response the data suggests that the resistivity decreases since an increase in voltage accompanies the increased output of current.

⁽²⁾The numbers in parenthesis refer to the list of references appended to this paper.

The curve in Figure 4 shows that there are two distinct rates of voltage decay indicating that the ability of the ions to polarize in the coating is changed after a certain length of radiation exposure time.

The curve in Figure 3 deviates initially from the exponential slope. This suggests that the ions are not initially diffusion limited and that surface conduction might take place due to contamination on the surface of the coating. The surface of aluminum oxide is strongly hydroxylized which might contribute to this effect.⁽³⁾ The dark current reactions seem unaffected, however, after a similar radiation exposure.

Water is present in the highly absorbent coating even after prolonged bakeout. As the photo-response progresses the coating dehydrates and this seems to be the dominating factor in attenuating the current and voltage output. This is supported by the fact that, at the conclusion of testing, the vacuum pump was shut off and the pressure in the chamber was allowed to rise slowly due to small leaks in the system. At 10^{-3} torr the voltage and current values were higher than the final values observed during the testing schedule performed at 10^{-7} torr. At the cathode, equation (1) suggests that along with the creation of aluminum ions, impurities in the aluminum alloy electrode would be mobilized via a related mechanism, and made available to influence optical properties. Proceeding toward the anode, dehydroxylation of the aluminum oxide according to the scheme



presents sites for charge transfer absorption. The doubtful oxidation states of the impurities are conducive to color center formation. The manner in which the impurities function is important.

GENERAL CONCLUSIONS

The decay of the conductivity processes of this aluminum oxide-potassium silicate coating is related to the dehydration of water from this coating. The conduction of the coating is normally ionic but when the coating is stimulated by UV, hole conduction is the predominant contributing factor to the conduction process. The coating is self

⁽³⁾The numbers in parenthesis refer to the list of references appended to this paper.

polarizing and is enhanced due to UV radiation. Under UV exposure, dehydroxylation of the surface of the coating coupled with the release of impurities at the cathode and their subsequent diffusion may combine these effects to form color centers in the coating, with a net resultant increase in absorptivity.

ACKNOWLEDGEMENTS

The author is indebted to Dr. John B. Schutt for his illuminating discussions and helpful suggestions. The author is also grateful to Charles M. Shai for preparing and applying the coating and to Robert N. Sheehy and his group for applying the gold electrodes to the coating.

REFERENCES

1. Latimer, W. M., "Oxidation Potentials", Prentice-Hall, New York 1952, p. 348
2. Ruff, I., J. Phys. Chem. 69, 3183 (1965)
3. Carter, J. L., Lucchesi, P. J., Corneil, P., Yates, D. J. C., and Sinfelt, J. H., J. Phys. Chem. 69, 3070 (1965)

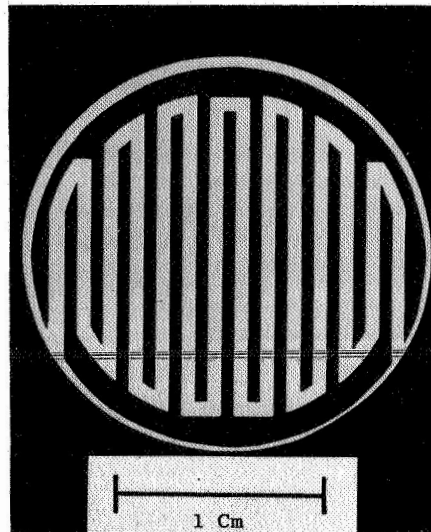


Fig. 1—Configuration of vapor deposited gold electrode.

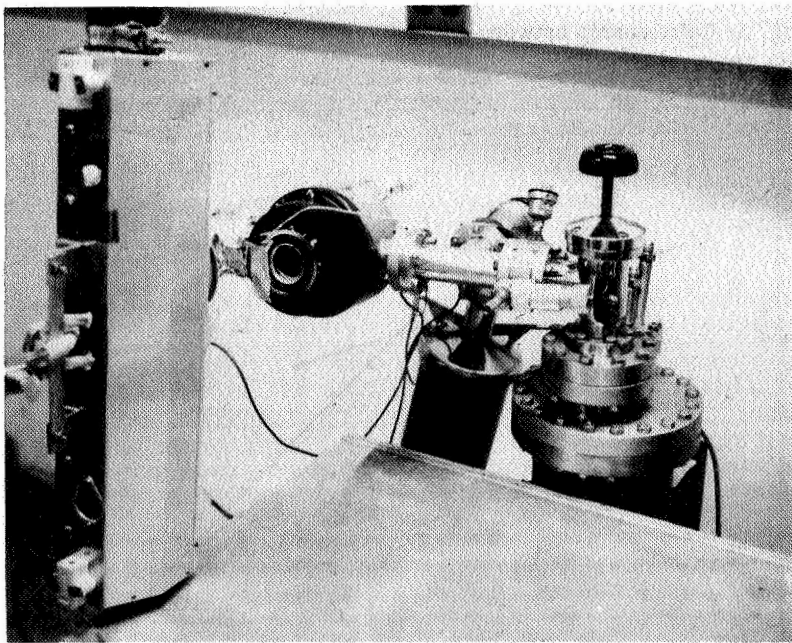


Fig. 2—Photograph of experimental apparatus; sample chamber and light source.

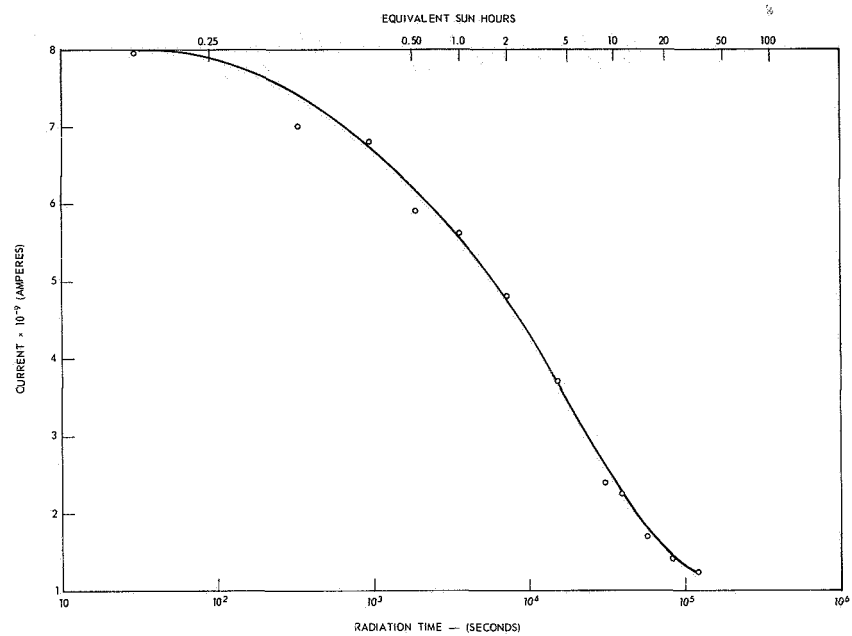


Fig. 3—Relationship between UV photo-response of current vs. radiation time.

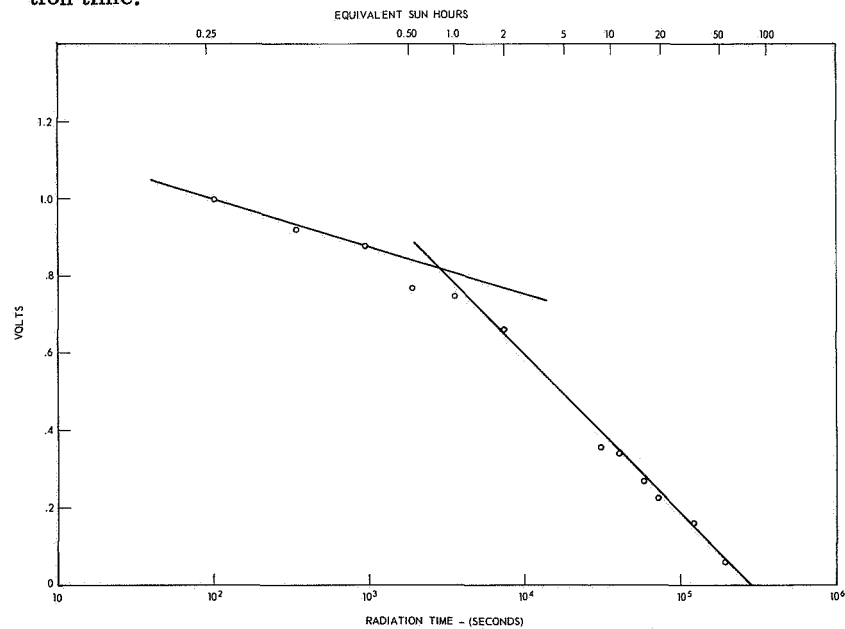


Fig. 4—Relationship between UV photo-response of voltage vs. radiation time.

Paper No. 28

PLANS AND STATUS OF NMAB ad hoc COMMITTEE ON TESTING FOR
PREDICTION OF MATERIAL PERFORMANCE IN STRUCTURES AND
COMPONENTS

Robert S. Shane

National Materials Advisory Board, National Research Council -
National Academy of Sciences, Washington, D. C.

ABSTRACT: National Materials Advisory Board - National
Research Council - National Academy of Sciences - ad hoc
Committee on "Testing for Prediction of Material Performance
in Structures and Components" - Interim Report

At the request of the Office of the Director of Defense
Research and Engineering, the National Materials Advisory
Board of the National Academy of Sciences has undertaken to
review "Testing for Prediction of Material Performance in
Structures and Components".

The basic purposes of the study have been identified as:
(a) make a selective survey of the needs for new and/or
improved predictive (including accelerated) testing techniques;
(b) consider predictive methods for forecasting the performance
of materials in structures and components under combined
stresses in service; (c) identify the factors of predictive
testing and explore approaches for development of methods and
techniques of predictive testing; (d) appraise the benefits of
predictive testing as well as the risks of predictive testing;
(e) provide guidance in establishing a policy for Government
and/or Industry interaction; (f) recommend mechanisms for
implementing this policy.

An ad hoc Committee has been appointed and convened. The
principal problem areas appear to be (a) interaction phenomena,
(b) design of multi-factor tests which forecast definitively
the behavior of structures and components in the presence of
known or foreseeable failure modes, involving materials
(c) lack of systematic accumulation of existing information so
that gaps in needed knowledge become apparent and remedial
action can be taken before design choices are irrevocably made,

(d) peripheral failure modes are frequently overlooked.

NMAB plans to co-sponsor the ASTM National Symposium on Predictive Testing, Anaheim, California, April 21-23, 1971.

KEY WORDS: combined environments, components, material performance, predictive testing, structures

(Complete paper not available)

Paper No. 29

MONITORING SERVICE TESTING BY NONDESTRUCTIVE TESTING

Robert W. McClung

Oak Ridge National Laboratory, Oak Ridge, Tennessee

ABSTRACT: Applications of nondestructive testing techniques to monitor tests include the use of x-rays with both film and television detection to monitor thermal cycling of fuel rods, neutron radiography on irradiation experiments, eddy-current measurement of space interval between components, and interim monitoring by ultrasonics of the wall thickness of a vessel in a reactor experiment. Studies during fabrication development include multiple interim measurements of compaction density of fuel rods and impregnation density of graphite using quantitative gamma and x-ray attenuation as well as use of eddy-currents to monitor changes in quality of sodium bonding in a fuel rod. Recommended approaches include the use of eddy-current methods to monitor changes in electrical properties, dimensions or flaw character, ultrasonics to measure changes in elastic properties, dimensions or flaw character, penetrating radiation to observe or measure changes in density, or dimensions and other forms of energy for similar applications.

KEY WORDS: compaction density, eddy current measurements, fuel rods, impregnation density, monitor tests, neutron radiography, ultrasonics, x-rays

(Complete paper not available)